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**SPECTROSCOPIC STUDIES
OF THE
HYDROGEN-CHLORINE FLAME**

by

Gonzalo Pizarro

**A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment
of the
Degree of Master of Arts**

**Western Michigan University
Kalamazoo, Michigan
August 1975**

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Gonzalo Pizarro

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INTRODUCTION

Since Bunsen and Kirchhof (1) constructed their first spectroscope in 1859, chemists have been interested in developing better flames as excitation sources for flame spectroscopy. Various flames have been investigated for improvements in the energy necessary to cause excitation of the atoms. In general, the hotter the flame, the greater the energy available. Table I shows some important characteristics of several flames.

These excitation sources have been used in atomic absorption, atomic emission and atomic fluorescence spectroscopy, but as Table I indicates, they exhibit their own characteristic bands which are particularly troublesome when the species under study exhibits its signal in one of these regions. Another problem associated with some of these flames is the formation of refractory oxides which often do not emit significant radiation. Thus it is difficult to study elements forming those oxides. Typical examples are many of the rare earth metals.

It would be desirable then to develop a new flame in which no interfering bands appear and in which the formation of refractory oxides is eliminated. The hydrogen-fluorine flame has been reported (2) as a valuable excitation source, and although it has given greater sensitivities when compared with the acetylene-oxygen or hydrogen-oxygen flames, the corrosiveness and toxicity of the combustion products limit its use. Another possibility is a hydrogen-chlorine flame; its combustion products are also corrosive and toxic, but not nearly as

severe as those of the hydrogen-fluorine flame.

Table I. Characteristics of some flames.

Fuel	Oxidant	Burning Velocity (cm/sec)	Temperature (°C)	Interfering Bands	Ref.
Hydrogen	air	440	2100	OH	2,4
Hydrogen	oxygen	3680	2780	OH	2
Hydrogen	N ₂ O	390	2950		3
City gas	air	55	1840	<div style="display: flex; align-items: center; justify-content: center;"> <div style="font-size: 4em; margin-right: 10px;">}</div> <div> OH, CH C₂, CO O₂ </div> </div>	2,4
City gas	oxygen		2740		
Methane	air	69.8	1875		
Methane	oxygen	5502	2677		
Ethane	air	85.6	1895		
Propane	air	82.1	1925		
Propane	oxygen		2850		
Butane	air	82.6	1900		
Butane	oxygen		1895		
Acetylene	air	266	2397		
Acetylene	oxygen	2480	3100		
Acetylene	N ₂ O	160	3250		3
Cyanogen	air	20	2600		3
Cyanogen	oxygen		4550	CN, NO C ₂ , CO	2,4,5
Hydrogen	fluorine		4000		
Hydrogen	perchloryl- fluoride		3300	OH, ClO	2,4

The applicability of the hydrogen-chlorine flame in flame spectroscopy was the subject of our investigation. This flame should not produce those interfering bands present in other flames and therefore should facilitate the analysis of many different elements which are difficult to analyze using conventional flames. Obviously hydrogen-chloride emission from the reaction product will be present, however these bands are located at 1950, 28600, and 29500 Å. This leaves the normal ultraviolet and the entire visible regions free from flame band emission. No oxides should be formed as products in the reaction, although chlorides will be formed. In many cases these chlorides will be less stable than their corresponding oxides as evidenced by their bond and dissociation energies (6). It should be mentioned that the hydrogen-chlorine flame is not as hot as many other flames but the lower excitation energies and the preferred background characteristics might offer significant advantages in its analytical application. Consequently one might expect that this flame could be particularly useful in the study of those elements which tend to form refractory oxides in other flames.

Historical

The hydrogen-chlorine system has been studied since last century. During the 1850's Bunsen and Roscoe (7) were interested particularly in its induction period, a phenomenon discovered by Draper some years before. In 1918 Nernst (8) suggested that the primary active centers of the photochemical reaction are the chlorine atoms formed in the

photochemical partition of chlorine molecules which react with hydrogen. Kondrat'ev (9) took this suggestion and proposed a radical-chain mechanism for the photochemical and thermal reactions of chlorine and hydrogen. The explosions produced by mixtures of chlorine and hydrogen have been studied, especially during the past century (10, 11).

The hydrogen-chlorine system as a flame was used by Mitscherlich (12) in 1864 to study different elements. In 1912 A. Harnack (13) made a comparative study of the oxy-hydrogen and chloro-hydrogen flames and made the first photographic measurements of the latter system. In 1937 T. Kitagawa (14) studied the emission spectrum of the flame and measured 18 emission bands in the region between 5590 and 6500 Å, which were not observed in this investigation.

Different values for the burning velocities and temperatures for this flame have been reported as shown in Table II.

Table II. Burning velocities and temperatures reported for the hydrogen-chlorine flame.

Burning velocities (cm/sec)	Temperatures °K	Conditions	Ref.
	2500	48% mole chlorine	15
405		40% chlorine	16
	1730		17
357	1126	H ₂ /H ₂ +Cl ₂ =0.650 46% nitrogen	18
236	1383	H ₂ /H ₂ +Cl ₂ =0.528 46% nitrogen	18
	2075		19

In 1969 W. K. Johnston (19) studied the hydrogen-chlorine flame as a potential source for excitation in flame photometry. He obtained the emission spectra of several elements in the region from 2500 to 6500 Å by aspirating ethanolic solutions of salts into the flame. The results were compared with those obtained in a hydrogen-air flame. Some of the elements gave comparable emission intensities in either system while other elements gave molecular chloride bands such as with copper where the band was unusually strong.

EXPERIMENTAL

Instrumental

Fuel-oxidant system: The compressed hydrogen was maintained at 25 p.s.i. by a two-stage regulator (Linde Company, R 219) at the cylinder while flow was controlled by a Matheson 605 flowmeter with a stainless-steel float. The chlorine, on the other hand, was regulated manually with a Matheson monel needle valve at the cylinder and a Matheson monel 604 flowmeter with a pyrex float.

Burner: Due to the corrosive atmosphere produced by the oxidant-fuel reaction, it was necessary to construct the burner from a material which was resistant to attack by chlorine and hydrogen chloride. The material chosen was monel and the design was based on the Ditric Corporation's Model V-10S aspirator-burner. The basic dimensions are the same, however several modifications were deemed necessary. The outer and inner parts are threaded to permit assembly of the unit. A circular plate with an o-ring seal is then attached to prevent leakage. The capillary was constructed from a three inch number 24 gauge stainless-steel syringe needle, in such a way as to permit adjustment of its height with respect to the tip of the burner. This is easily done by adjusting its position in the inner jacket. A drawing of the excitation-aspiration system can be seen in Figure 1.

Spectrometer: The unit used in these studies was a Jarrell-Ash Atomic Absorption-Flame Emission Photometer Model 82-536 with interchangeable fixed slits. This system consists of a 0.5-meter Ebert Scanning

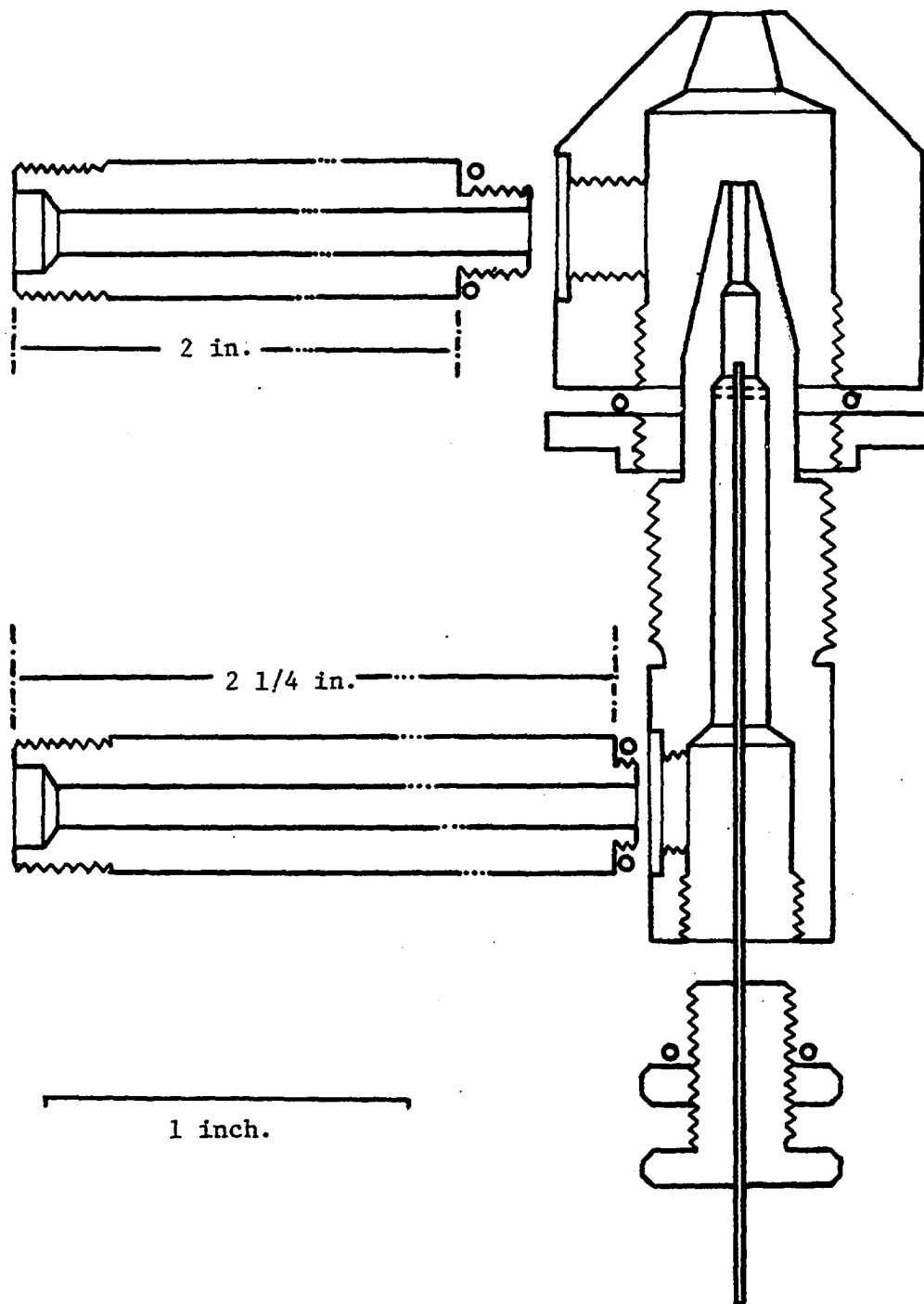


Figure 1. Burner-Aspirator System

Spectrometer with a 150 mm. diameter concave mirror and a replica grating having 1180 grooves per mm., and blazed at 3000 Å. Its resolution is 0.2 Å in the first order and the effective aperture ratio is $f/8.6$. The detector used with this monochromator was a Jarrel-Ash number R212 photomultiplier tube having an S-5 response. The power supply for the photomultiplier was a Model 244 High Voltage Supply manufactured by Keithley Instruments. The signal from the detector was fed to a Model 112 preamplifier and then to a Model 122 lock-in amplifier both manufactured by the Princeton Applied Research Corporation.

Chopper-Reference Source System: The circuit diagram of the reference signal source for the lock-in amplifier is shown in Figure 2. In reality it is nothing more than dual voltage regulated power supplies sharing a common full-wave rectifier. Line voltage is stepped down by means of transformer T which now supplies the full-wave rectifier comprised diodes D_1 , D_2 , D_3 , and D_4 . The positive output of the rectifier is located between diodes D_2 and D_4 with the common being located at the junction of diodes D_1 and D_3 . Capacitor C_1 serves as a filter capacitor to reduce ripple voltage from the full-wave rectifier. The regulation circuit, comprised of P_1 , R_1 , R_3 , C_2 , Q_1 , C_4 and R_5 , is exactly complimented by another regulation circuit comprised P_2 , R_2 , R_4 , C_3 , Q_2 , C_5 and R_6 . Both regulation circuits operate in the same manner. They function by maintaining the negative output of the power supply at preset voltage levels, determined by P_1 , relative to the common positive output. The network of resistors

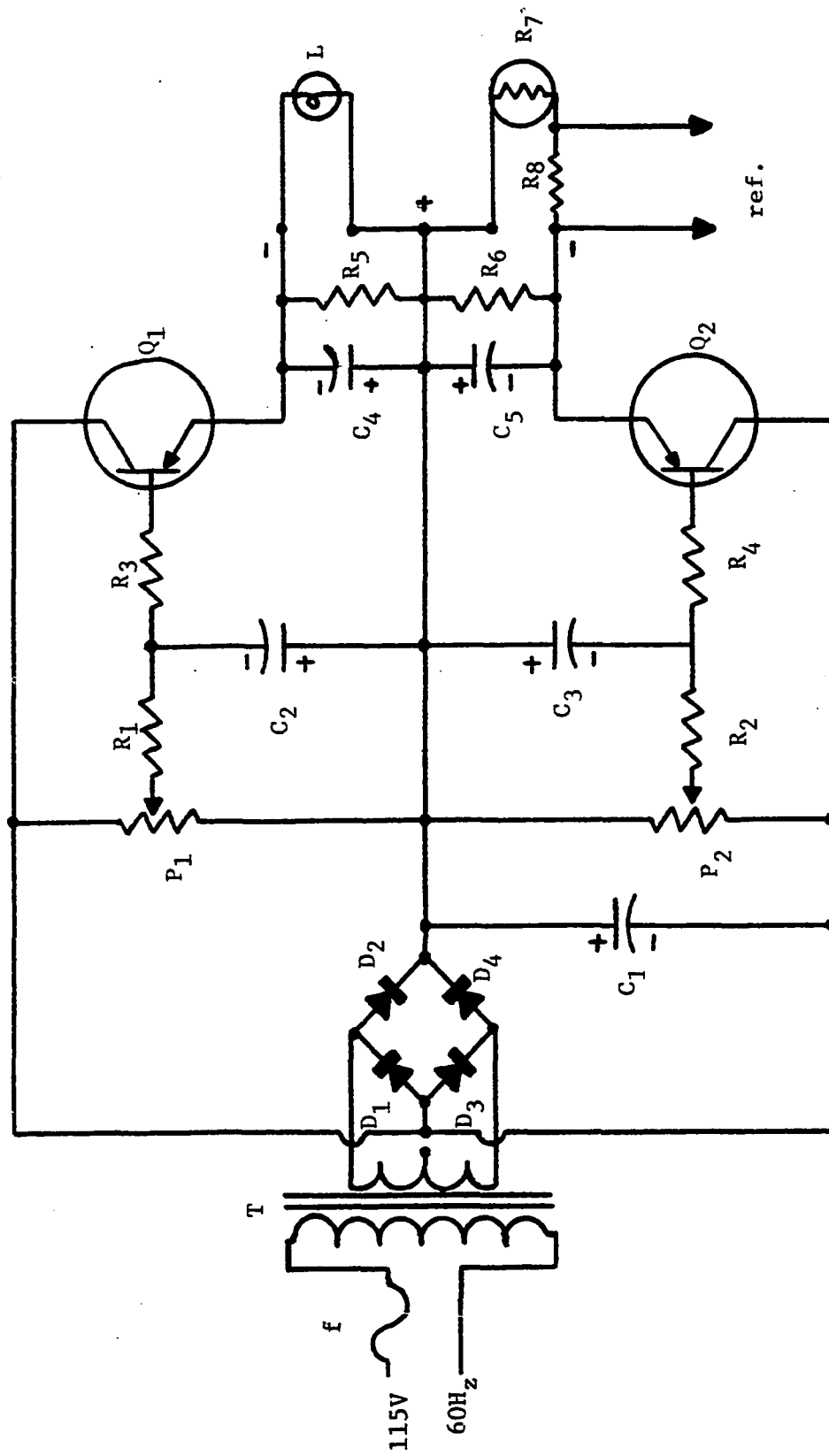


Figure 2. Chopper-Reference Source System.

P_1 , R_1 , R_3 and R_5 establish the emitter-base voltage of Q_1 which controls the collector-emitter current. If the output voltage were to drop below the preset value, this would reduce the emitter-base bias voltage, and thus restricts the collector-emitter current to such a value as to allow the output voltage to reestablish its desired preset value. On the other hand if the output voltage were to increase above its preset value, this would cause the collector-emitter to increase until the preset output voltage was reestablished. Capacitors C_2 and C_3 serve merely to further reduce the power supply ripple voltage to transistors Q_1 and Q_2 respectively. Capacitors C_4 and C_5 are provided to shunt high frequency pulses and thus prevent the outputs from undergoing oscillation. Both regulated outputs can be varied independently between 0 and 25 volts d.c. and are nominally operated at 6 volts.

One of the outputs provides power for the excitation lamp L, while the other serves as a source for the photoconductive cell R_7 and its series resistor R_8 . The lamp and photoconductive cell are physically arranged so that the light from the lamp falls on the photocell. This configuration is in turn arranged such that the synchronous drive mechanical chopper which chops the optical signal from the flame also chops the light from lamp L. The chopping effect produces a pseudo-square wave voltage waveform across resistor R_3 which is then utilized as the reference signal source for the lock-in amplifier. Mechanically slaving the reference signal to that of the flame signal insures that variations in chopper speed will not result in

loss of amplifier sensitivity due to frequency drift once initial phasing has been achieved. The following is a parts list for the chopper reference source:

f - fuse, 1/2 amp. 3 AG (Little Fuse)
 T - Transformer, 20vCT, 1A (Stancor P 8604)
 D₁, D₂, D₃, D₄ - Diodes (General Electric, 1N315)
 C₁ - Capacitor, electrolytic, 1000 mfd. 50v (Cornell Dubilier)
 P₁, P₂ - Potentiometer, 5K Ω , 1/2 w, (Allen-Bradely, Type J)
 R₁, R₂ - Resistor, 470 Ω , 1w (IRC)
 C₂, C₃ - Capacitor, electrolytic, 500 mfd. 50v (Sprague)
 R₃, R₄ - Resistor, 22 Ω , 1w (IRC)
 Q₁, Q₂ - Transistor, PNP (Texas Instruments R265 A)
 C₄, C₅ - Capacitor, disk 0.1 mfd. 50v (CRL)
 R₅, R₆ - Resistor 330 Ω , 1w (IRC)
 L - Lamp, bayonet, (General Electric, No. 44)
 R₇ - Photoconductive Cell, CdS (Solar System R3)
 R₈ - Resistor, 220 Ω , 2w (IRC)

Time Averaging Unit: A very important component of the system was the time averaging unit which operates upon the basic premise that noise is random over a period of time. The positive excursions will be offset by an equal number of negative excursions of comparable magnitudes. The signal on the other hand will always be positive. Therefore by adding time increments of the reading, the noise will tend to be cancelled out while the signal will continue to be additive. This entire process can be accomplished simply by integrating the reading over a prescribed time period. However in order to achieve any degree of precision for successive measurements, the integration time must be precisely reproduced. Longer integration times should therefore tend to improve the signal to noise ratio. This is indeed the case up to the point where the uncertainty associated with the longer time periods begins to affect the precision.

The circuit used for time averaging in this investigation is shown in Figure 3. The switching sequence for the circuit may be seen in Figure 4. The entire circuit was constructed from components of a Heath Model EU- 801A Analog-Digital Designer module. This circuit may be considered to be comprised of two major parts, an analog and a digital section.

The analog section is comprised of the signal input, FET switches S-1, S-2, and S-3, resistors, R_1 , R_2 and R_3 , operational amplifiers OA-1, and OA-2, capacitor C-1, and the signal output. Operational amplifier OA-1 and resistors R-1 and R-2 function as a gain amplifier to adjust the input signal to a level appropriate for the integrator. Resistor R-3, capacitor C-1, and operational amplifier OA-2 serve as the integrator.

The digital section of the circuit is comprised of four basic units, the gating control, the counter, the monostable delay, and the switch control. The gating control includes NAND gates N-1 and N-2, while the counter is made up of flip-flops F-1, F-2, and F-3. The monostable unit includes NAND gates N-6 and N-7, and capacitor C-2. The switch control section is comprised of NAND gates N-3, N-4 and N-5, and flip-flops F-4, F-5, and F-6.

The operation of the circuit simply resets the integrator to zero, then connects the input while beginning the count sequence. When the preset count has been achieved, the input is disconnected while output is connected.

More specifically the time base generator (Heath Timing Module,

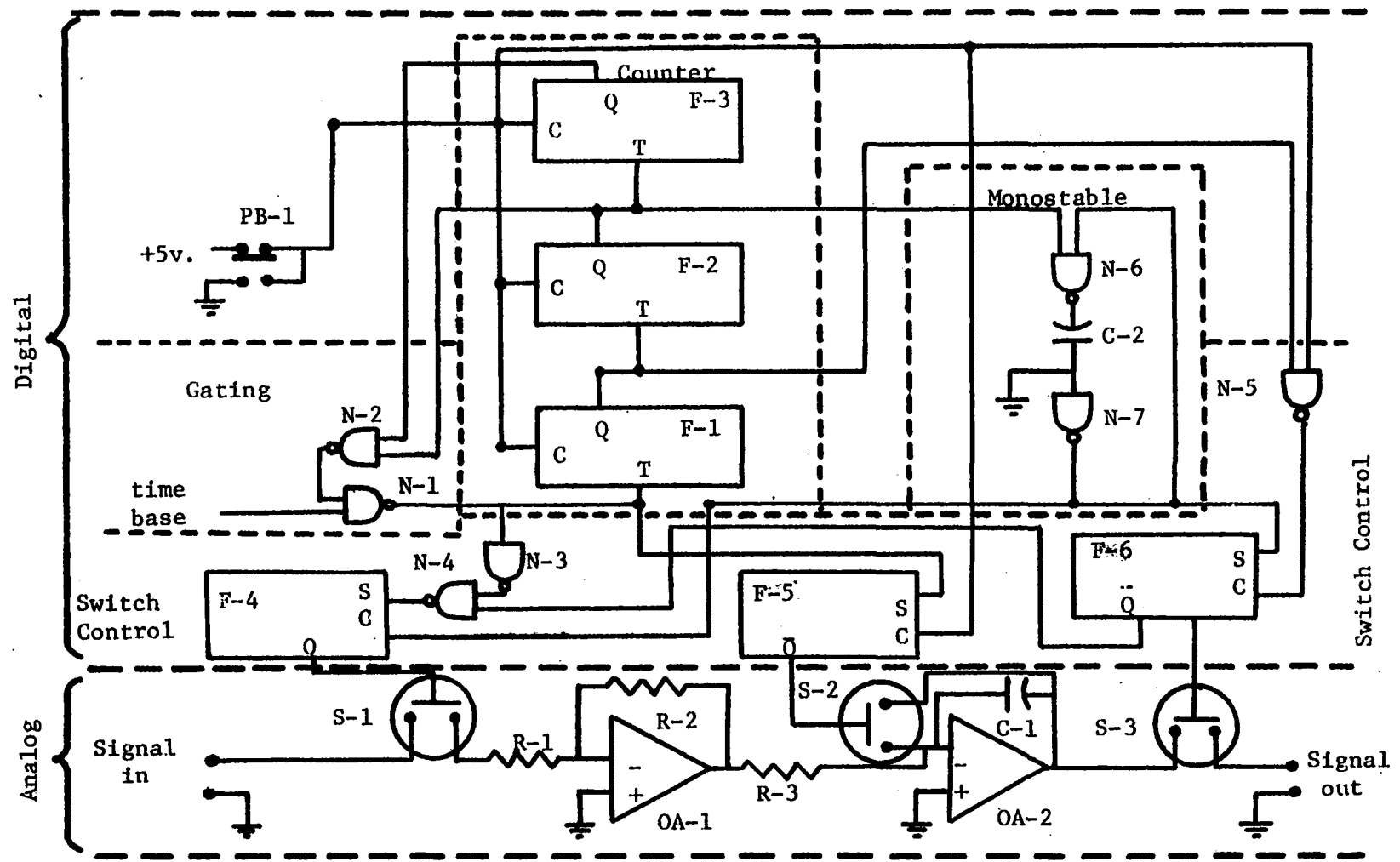


Figure 3. Time averaging circuit

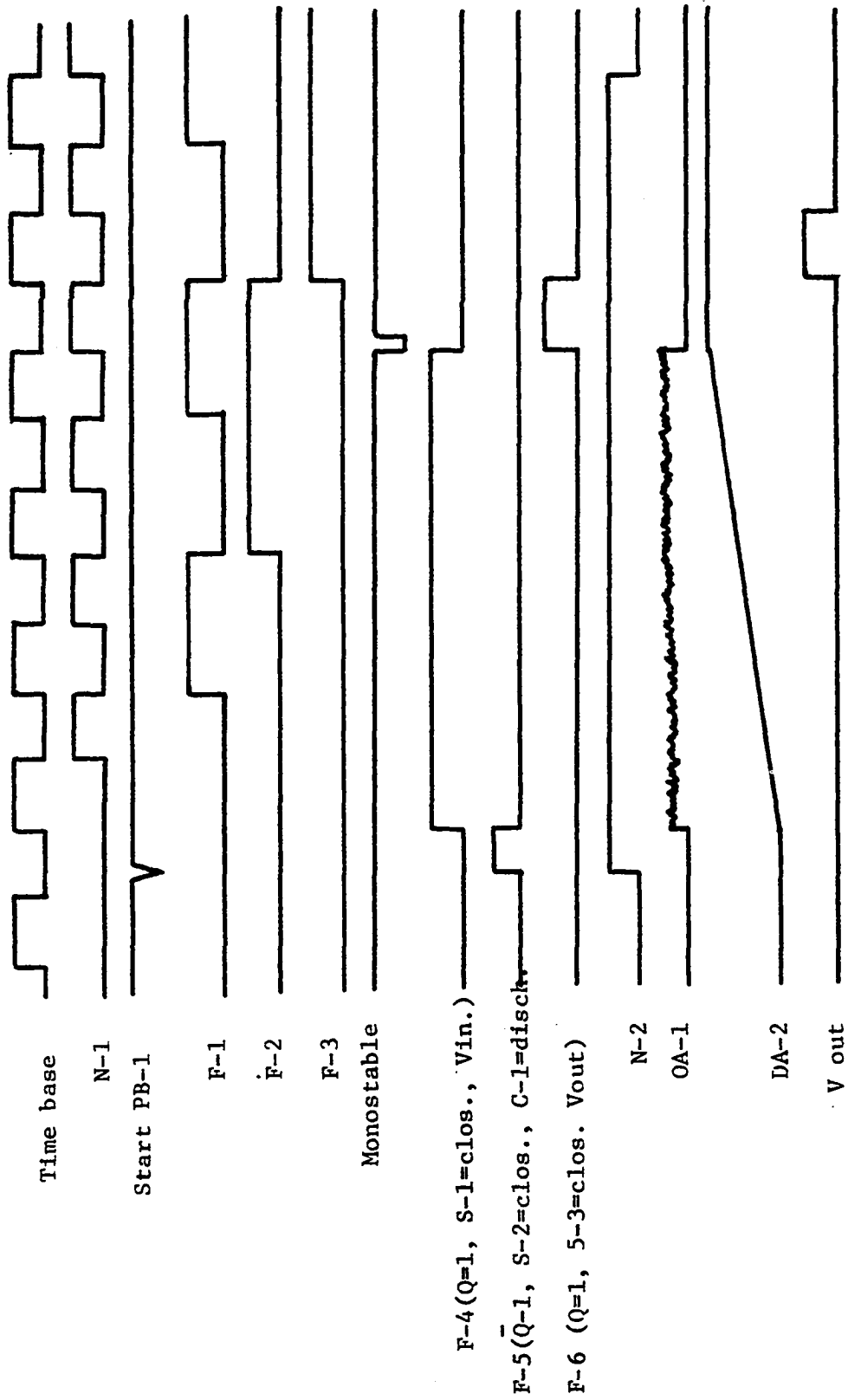


Figure 4. Switching sequence

Model EU801-13) supplies to the gate a continuous train of pulses whose frequency can be set from 0.1 Hz to 1 KHz. Nominally the frequency used was about 0.25 Hz. When PB-1 is activated, the counter is cleared and set to zero. Simultaneously switches S-1 and S-3 are opened while S-2 is closed in order to clear and reset the integrator. With next time base pulse the gate is opened at which time S-2 is opened, S-1 is closed connecting the input, and the counter begins counting. When the fourth pulse, resulting from the time base input, is read, the monostable is then activated. The monostable output in turn opens S-1, disconnecting the input, and simultaneously closes S-3 thereby applying the integrated signal to the signal output. The counter continues to count until an eight count is read by the counter, at which time the gate is closed and S-3 is opened removing the integrator from the output. This then completes the cycle and the system is again ready to be reinitiated by activation of PB-1. Finally the output from the time averaging unit was displayed on a Honeywell Electronik 194 Laboratory recorder.

The gain of OA-1 and time base frequency must be compatible so as not to saturate the integrator during the integration time. Integration times are easily selected with the variable frequency control on the time base generator.

The reproducibility of the time base generator was 0.2%, however greater precision could easily be achieved by utilizing a precision crystal oscillator with a reproducibility of 0.0001% or better. If this were done, it would also necessitate the use of the highest qua-

lity capacitors available so as to prevent errors due to leakage.

Reagents

The elements chosen to be investigated in the hydrogen-chlorine flame were: aluminum, arsenic, barium, boron, cesium, copper, iron and silicon. Solutions containing these elements were prepared as follows:

Aluminum: 5.00 grams of purified aluminum (Baker analyzed) was dissolved in hydrochloric acid and diluted to 500 ml to give a solution containing $1.00 \times 10^3 \mu\text{g/ml}$. From this, other solutions containing 8.00×10^3 , 6.00×10^3 , 4.00×10^3 and $2.00 \times 10^3 \mu\text{g/ml}$ were prepared by appropriate dilutions. All the solutions were prepared in distilled water. Another solution comprised of 3.52 g. of lithium aluminum hydride (95%, Baker grade) was prepared in 250 ml. of anhydrous ether (Fisher Reagent ACS).

Arsenic: A stock solution containing $1.00 \times 10^5 \mu\text{g/ml}$ of arsenic was prepared by dissolving 56.50 ml. of arsenic trichloride (99%, Matheson-Coleman, $d^{20} = 2.163 \text{ g/ml}$) in alcohol and diluting to 500 ml. Other solutions containing 8.00×10^4 , 6.00×10^4 , 4.00×10^4 and $2.00 \times 10^4 \mu\text{g/ml}$ were obtained from the original stock solution using alcohol as the solvent.

Barium: 1.78 grams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker analyzed) was used to prepare a stock solution containing $1.00 \times 10^3 \mu\text{g/ml}$ by dissolution in 500 ml. of distilled water. Other solutions containing 500, 400, 300, 200, and 100 $\mu\text{g/ml}$ were subsequently prepared for this stock solution

using distilled water.

Boron: 14.3 grams of boric acid (Mallinckrodt, ACS) was dissolved in concentrated ammonium hydroxide and diluted to 500 ml. with distilled water to give a stock solution containing $5.00 \times 10^3 \mu\text{g/ml}$. Solutions containing 4.00×10^3 , 3.00×10^3 , 2.00×10^3 , and $1.00 \times 10^3 \mu\text{g/ml}$ by appropriate dilution of the stock solution with distilled water were prepared. Also a solution of boron trifluoride ether complex (98%, Matheson-Coleman), was used to prepare a stock solution containing $5.00 \times 10^3 \mu\text{g/ml}$ in ether. Subsequent dilutions were made with diethyl ether to obtain concentrations of 1.00×10^3 , 800, 600, 400 and 200 $\mu\text{g/ml}$.

Cesium: 0.636 grams of purified cesium chloride (Fisher Certified) was dissolved in 500 ml of distilled water to obtain a stock solution containing $1.00 \times 10^3 \mu\text{g/ml}$. From this solution several dilutions containing 500, 400, 300, 200 and 100 $\mu\text{g/ml}$ were made.

Copper: A stock solution of copper was made by dissolving 64.8 mg of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Mallinckrodt, A.R.) in distilled water and diluting to 500 ml. to give a stock solution containing 420 $\mu\text{g/ml}$. Subsequent dilutions led to solutions containing 40.0, 30.0, 20.0, 10.0 and 5.00 $\mu\text{g/ml}$. All solutions were prepared in distilled water.

Iron: 1.45 grams of sublimed anhydrous ferric chloride (Fisher, Purified) was used to prepare the 500 ml of a 998 $\mu\text{g/ml}$ iron solution. From this stock solution others containing 100, 80.0, 60.0, 40.0 and 20.0 $\mu\text{g/ml}$ were prepared.

Silicon: 10.0 ml of tetramethyl silane (Aldrich, Sp. Gr. $^{19}_4 - 0.648$)

was dissolved in 500 ml of carbon tetrachloride (Fisher A.C.S.) to obtain a stock solution containing $4.13 \times 10^3 \mu\text{g}/\text{ml}$ of silicon.

Spectrum Analysis

Although different flow rates for both the hydrogen and the chlorine were tried, it was found that under the experimental conditions and instrumental limitations, the optimum flow rates were: 1.17 l./min for chlorine, and for hydrogen 6.71 l./min, 6.33 l./min, 6.16 l./min and 7.00 l./min, for aqueous, ethanolic, ether, and carbon tetrachloride solvents respectively.

Density, viscosity, and surface tension variables caused the analytes to be aspirated into the flame at different rates depending on the solvent used. Rates of 0.94, 1.13, 1.5, and 0.65 ml/min. for aqueous, ethanolic, ether, and carbon tetrachloride solutions respectively were obtained.

Using entrance and exit slits of $150 \mu\text{m}$, the spectrum of each element was obtained from 2000 to 6000 Å, except for arsenic which was measured from 1850 to 6000 Å. The wavelength was scanned at 500 Å/min. with an amplifier sensitivity of 20.0 mv. and a time constant of 10.0 seconds. The photomultiplier power supply was operated at 460 volts while the chart speed of the recorder was 1.00 inch./min.

Once the spectra were obtained for each element, the most sensitive line or band was determined. Fixed wavelength measurements of this line or band were made with the amplifier sensitivity of 5.00 mv., and the time constant setting at 1.0 second. The integration

times used were 19.0, 24.0, or 29.0 seconds depending on the intensity of the signal. The other instrumental parameters were maintained as they were during the spectral scans.

RESULTS

The flame background exhibits only the OH bands when measured between 2000 and 6000 Å. Also lines of mercury resulting from the fluorescent lights were observed. For this reason all the spectra were obtained with the room lights off to prevent this interference during spectral scans. The flame background can be seen in Figure 5. With the exception of copper which was examined in a region where the room lights interfere, fixed wavelength measurements of the other elements were made with the lights on. The results obtained for the various elements studied are contained in Table III.

Table III. Fixed wavelength measurements.

Element (λ)	Concentration (mg/ml.)	Relative ₁ Intensity	Number of Determinations	Coefficient of Variation
Al ² (3961 Å)	10.0	8.4	4	8.30
	6.00	5.2	4	4.15
	2.00	2.5	4	17.7
Al ³ (3961 Å)	6.00	38.5	4	0.73
	4.00	33.1	3	0.85
	2.00	21.6	5	1.67
As (1937 Å)	100	17.5	5	3.98
	60.0	12.9	5	4.99
	20.0	6.1	5	3.10

Table III, (Cont.)

Element (λ)	Concentration (mg/ml.)	Relative Intensity ¹	Number of Determinations	Coefficient of Variation
B^4 (5476 A) (BO_2 band)	50.0	41.8	5	1.20
	40.0	32.2	5	2.46
	3.00	22.9	5	2.37
	2.00	13.7	5	2.16
	1.00	4.8	6	18.5
B^5 (5476 A) (BO_2 band)	1.00	29.2	5	1.23
	0.800	26.9	5	2.08
	0.400	19.6	4	1.12
	0.200	16.6	4	3.01
Cs (4555 A)	0.500	21.2	5	1.42
	0.400	17.7	5	1.30
	0.300	12.7	5	4.49
	0.200	8.3	5	5.78
	0.100	4.3	5	8.60
Cu (4359 A) (CuCl band)	0.0400	26.5	5	2.53
	0.0300	21.5	5	3.53
	0.0200	14.6	5	10.6
	0.0100	5.6	5	22.1
	0.00500	1.1	5	12.7

Table III, (Cont.)

Element (λ)	Concentration (mg/ml.)	Relative ¹ Intensity	Number of Determinations	Coefficient of Variation
Ba (5535 A)	0.500	64.8	5	2.31
	0.400	57.4	5	1.61
	0.300	41.9	7	3.63
	0.200	23.6	6	5.36
	0.100	10.2	5	4.22
Fe (3720 A)	0.100	55.3	5	1.18
	0.080	46.7	5	1.99
	0.060	33.7	5	2.02
	0.040	21.5	5	1.81
	0.020	9.4	5	2.98
Si: No significant radiation				

¹Corrected for background emission with blank.

²As aqueous aluminum chloride.

³As lithium aluminum hydride.

⁴As aqueous boric acid.

⁵As boron trifluoride ether complex.

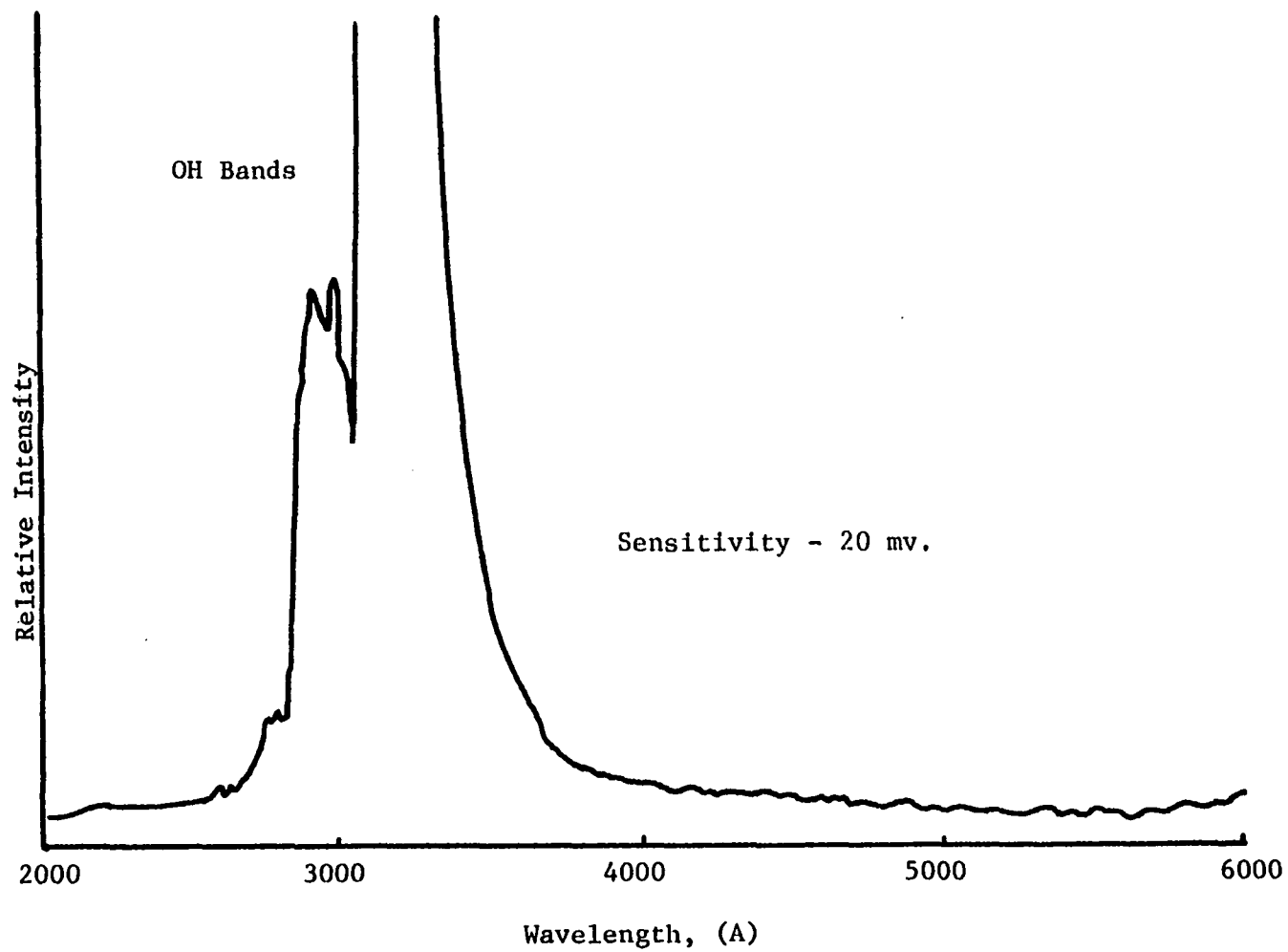


Figure 5: Background emission from the Hydrogen-chlorine flame.

DISCUSSION

The manner in which the reacting gases, hydrogen and chlorine, were introduced to the burner with hydrogen through the inner jacket and chlorine through the outer one, was necessary to avoid having the capillary being attacked by chlorine. In spite of this precaution the tip of the capillary was attacked through chlorine and hydrogen chloride diffusion, thus necessitating periodic adjustment.

An inverted flame such as described above can also offer some practical advantages relative to the flame mechanism occurring in the lower region of the reaction zone. Conventional flames generally have the aerosol introduced into the oxidant which then combines with fuel in the reaction zone. If this principle were applied to the hydrogen-chlorine flame we could see that through lateral diffusion the oxygen from the air would combine with hydrogen first according to reactions 1 and 2.



This causes the formation of OH radicals which would give rise to an increased flame background. However the inverted flame would have chlorine reacting with oxygen according to reactions 3 and 4.



In this case the OCl radical species is formed which contributes only diffuse band emission between 3700 and 4500 Å. Another aspect of the

conventional versus the inverted flame can be seen by considering vapor state reactions 5 and 6.



Reaction 5 describes the process occurring in the inner cone of a conventional flame using sodium as an example. NaX represents the molecular vapor necessary for the formation of atomic vapor (20), where X may be any anion present in the solution. The oxidizing environment of the chlorine increases the probability of chloride formation thus resulting in band emission from the metal-chloride species. Reaction 6 indicates how the same process would occur in the inverted flame. Here it is seen that when the molecular vapor finds itself in a reducing environment, the probability of the production of atomic vapor is enhanced. Consequently band emission is likely to be less predominant in the inverted flame. It is also known that the diffusion of the oxidant into the reaction zone in conventional flames creates a large amount of turbulence of the oxidant and fuel in the combustion zone (3) with a corresponding increase in noise. Since line emission is generally preferred due to its inherent greater sensitivity and in view of the preceeding discussion, the advantages of the inverted flame become obvious.

Although the flame background was not diminished, as had been anticipated, due to the presence of the OH bands, it was nevertheless superior to the background of most other analytical flames. Most flames contain not only OH bands but also CO, CH, C₂, N₂, C_x, and

numerous others as can be seen in Table I. The OH bands often occur due to the reaction of hydrogen with oxygen from the surrounding air. For this reason, sheaths of nitrogen and argon were tested. Nevertheless the bands remained, although a decrease in intensity was noted. Examination of gas specifications revealed that the hydrogen used contained as much as 1 and 3 p.p.m. of oxygen and water respectively. Removal of these impurities from hydrogen was attempted by using pyrolitic copper (BTS Catalyst, Badische Anilin and Soda-Fabrik AG.) and molecular sieves (Type 3-A, Linde). Molecular sieves were also used to remove water from chlorine. These efforts to eliminate the OH bands were generally unsuccessful. Thus it was decided to continue the study and simply to tolerate the existing OH bands for the course of this investigation since most of the elements to be studied exhibited the emission lines or bands of interest in regions where the OH bands would not interfere.

It is generally recognized that diffusion flames exhibit more noise than premixed flames (3) and the system under study in this investigation was not an exception. Signal to noise ratios of about 6.67 r.m.s. were initially observed making graphical averaging difficult. Therefore it was felt that a time averaging circuit could significantly improve the observed signal to noise ratio. Figure 6 shows a comparison of the recorder output with and without time averaging. The integration time using the time averaging unit was not the same for all the elements. As expected it was found that the shorter this time, the less precise were the results obtained, as can be seen in

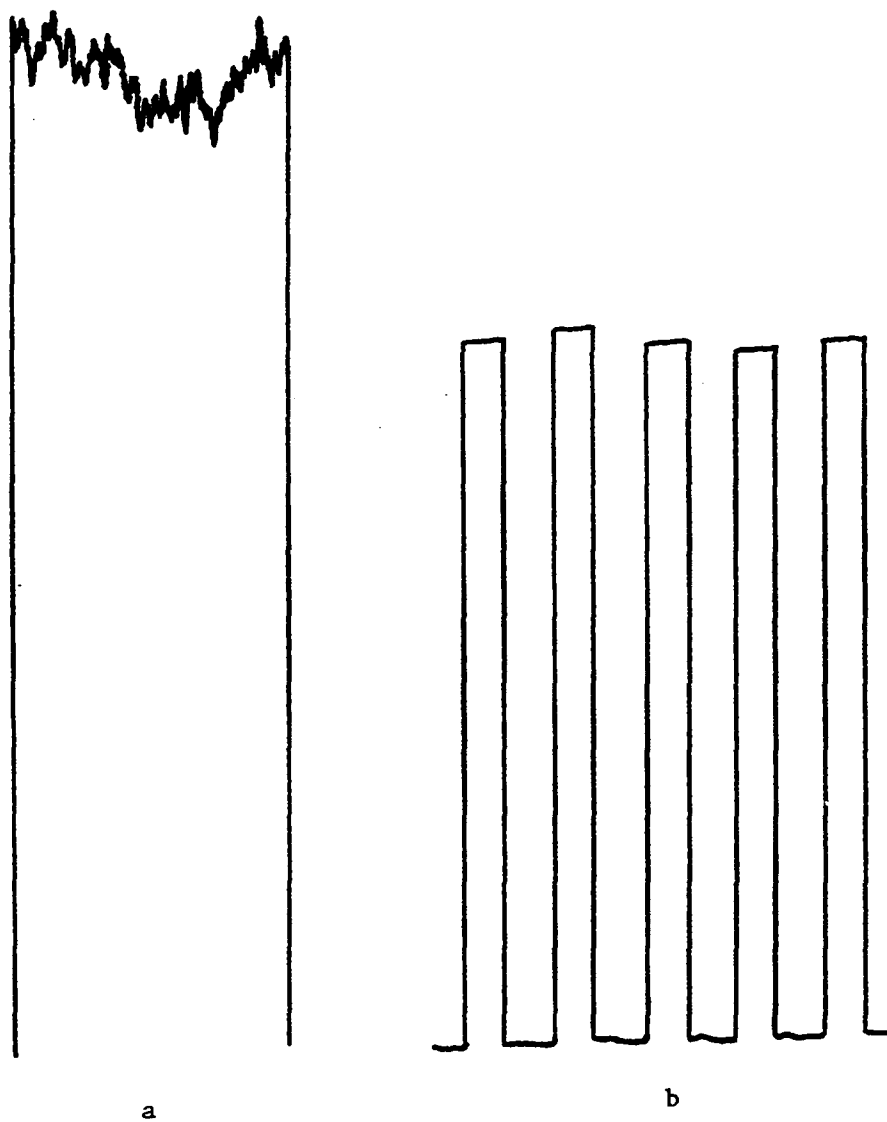


Figure 6. (a) Recorder output without integration, and (b) with integration.

Figure 7. Different integration times were necessary because the more sensitive elements exhibited signals sufficiently large to saturate the integrator of the time averager. The signal thus obtained for each concentration for a given element were used to plot the calibration curves. Least squares treatment of the data are shown in Figures 8 and 9 along with the integration time used for each element. The precision obtained for these measurements can be seen in Table III.

Calculation of Detection Limits

Winefordner and associates (21) proposed a very sophisticated method for calculating detection limits of flame emission measurements, based upon a series of experimental and instrumental parameters and in terms of the signal to noise ratio. The use of a time averaging circuit in the present investigation obviously precludes the observation of the peak to peak noise essential to the use of Winefordner equation. O. Menis and T. C. Rains (22) however recommend another procedure based on the random error observed in a sample which contains the element under study at a concentration sufficient to produce a signal five times as large as the background. The detection limit then becomes equal to plus or minus the standard deviation above background. This was the method used to calculate the detection limits shown in Table IV for the elements studied in this investigation.

In order for the reader to have some basis of comparison with which to judge the relative sensitivities observed in this investiga-

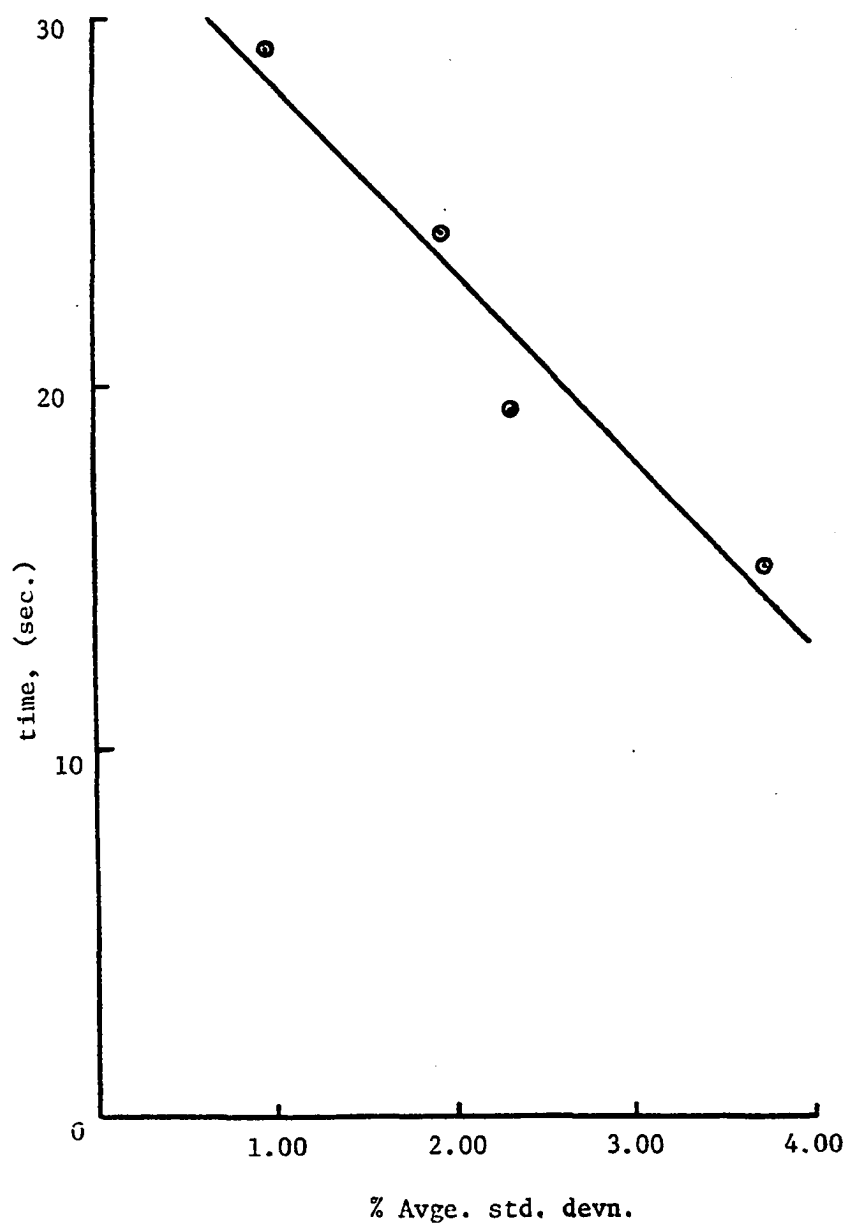


Figure 7. Effect of the integration time on the precision of the results.

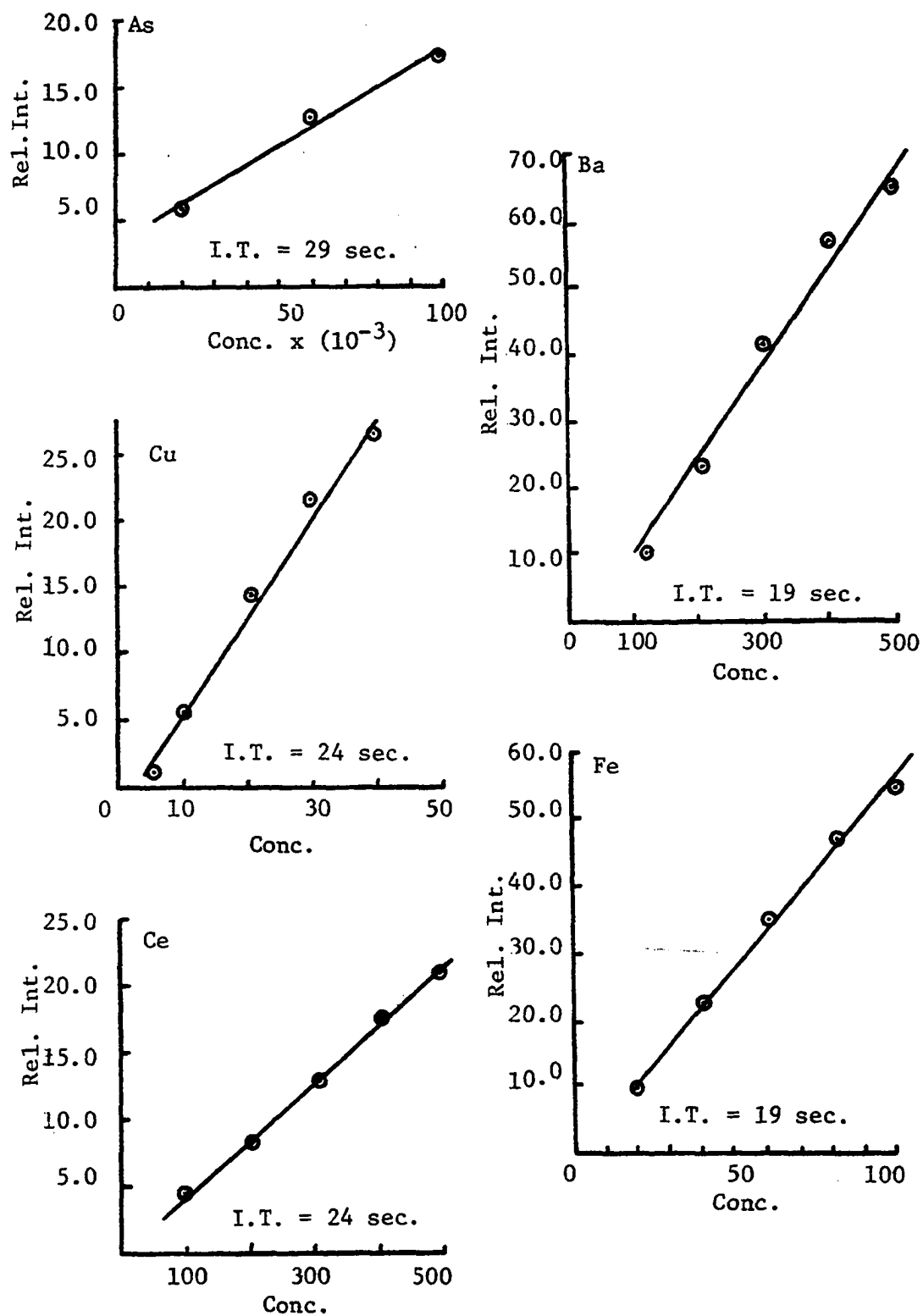


Figure 8. Calibration curves. (Concentration in $\mu\text{g/ml.}$)

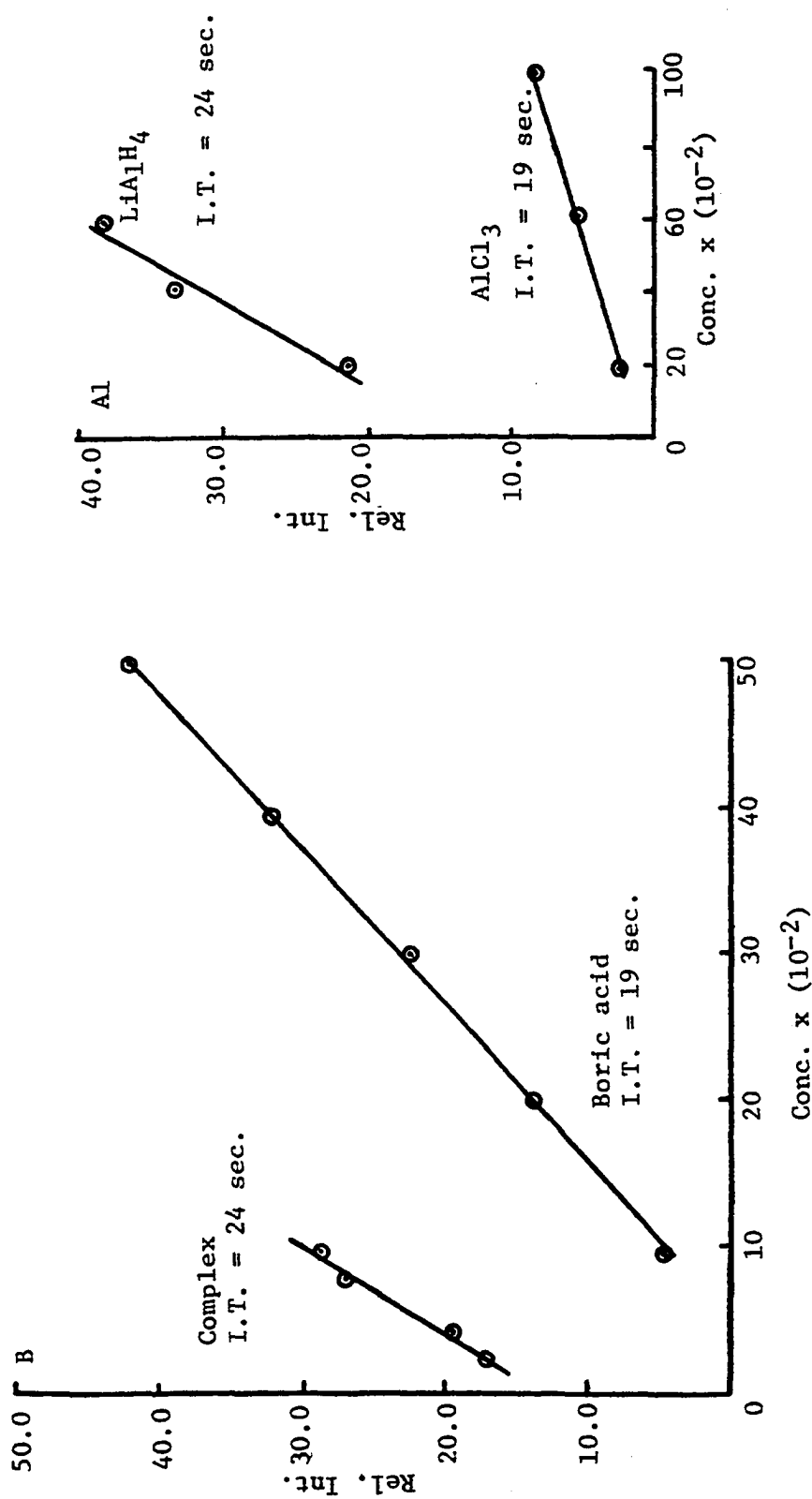


Figure 9. Calibration curves for boron and aluminum (concentration $\mu\text{g}/\text{ml.}$)

tion, Table IV has tabulated some typical emission sensitivities taken from a literature source (4). It should be noted that the observed detection limits found in this investigation are not intended to represent the minimum detection levels obtainable. It was not the purpose of this study to determine the minimum detection limits in the hydrogen-chlorine flame, but merely to investigate the presence of lines, bands and other characteristics of this flame. Consequently no efforts were made to optimize instrumental and experimental conditions for the purpose of achieving maximum sensitivity. It should suffice to say that had efforts been made to optimize the various parameters, enhancement of 10-fold or more should be possible.

With respect to the emission sensitivities tabulated in Table IV, one should be cognizant of the fact that there are no standardized criteria for expressing sensitivities in flame spectroscopy. The reason for this lies in the fact that in addition to the many varied ways of computing such limits, they are highly dependent upon factors such as fuel and oxidant selection, fuel and oxidant flow rates, solvent, type of amplification, type of detector, type of monochromator, type of burner, type of atomizer, and numerous other experimental and instrumental variables.

It should be pointed out that the detection limit for aluminum as lithium aluminum hydride is an estimated value in which it was assumed that the hydride was pure. In reality it contained hydrated aluminum oxide which was insoluble in diethyl ether. Thus, it is felt that the detection limit in this instance is significantly below

the value listed in the table, perhaps by as much as a factor of 2 or 3.

Table IV. Detection limits.

Element	Observed detection limits ($\mu\text{g/ml.}$)	Emission sensitivity ppm/% T (4)
Al (as AlCl_3)	1.66×10^3	0.4
Al (as LiAlH_4)	66.7	
As	5.77×10^3	Not listed
B (as boric acid)	84.6	3
B (as boron tri-fluoride ether complex)	33.4	
Cs	37.2	2
Cu	2	0.6
Ba	13	1
Fe	2.2	2.5
Si	Not detected	Not listed

Discussion of Results

Considering the basic phenomena involved in obtaining emission from a flame, one might expect to see some correlation between detection limits and thermodynamic data such as bond energies. Table V (6) lists bond energies for a number of the species studied in this investigation. It would appear to be a logical conclusion that low

bond energies should tend to enhance detection limits for atomic emission.

Table V. Strengths of Chemical Bonds (5)

Bond	Energy (Kcal/mole)
Al-Cl	117
Al-H	67
Al-O	106
As-Cl	Data not available
As-H	65
As-O	113
B-Cl	118
B-F	181
B-O	184
Ba-Cl	115
Ba-O	133
Cs-Cl	105
Cs-O	71
Cu-Cl	83
Cu-O	95
Fe-Cl	83
Fe-O	99
Si-C	104
Si-Cl	104
Si-O	187

One must, however, be careful in applying such simplistic arguments to predict results arising from the many complex and interrelated phenomena occurring in a flame. Solvent effects are well recognized as affecting emission signals. These effects are usually attributed

to density, viscosity, and surface tension variables which control the rate and efficiency of aerosol formation. Equally important are the effects of the solvent on temperature and the predominant flame mechanism. Kinetic factors can play significant roles in determining the production of molecular or atomic species in the flame. In spite of these complications bond energy considerations will play an important part in determining the nature and concentration of various species in the flame.

Inspection of Table V reveals that the bond energies of the Al-O and Al-Cl bonds are significantly greater than that of the Al-H bond. Since conventional flame spectroscopic measurements of aluminum are usually carried out in flames utilizing oxygen as the oxidant as well as using aqueous solutions, it is not surprising to find aluminum to be relatively insensitive to atomic emission analysis. The results obtained in this study tend to correlate well with the bond energies found in Table V, since aqueous aluminum chloride solutions gave much poorer sensitivities than did diethyl ether solutions of lithium aluminum hydride. Undoubtedly solvent effects do contribute significantly. However, it is difficult to ascertain to what degree they do so.

The relatively large bond energy of the As-O bond might in part explain the relative insensitivity of arsenic to atomic emission analysis by conventional flames. Only weak line emission for arsenic was observed when the trichloride was used and no significant radiation was found when a solution of arsine in chloroform was tested.

Although the As-H bond energy is not as high as that of the As-O, the preparation of arsine in appreciable amounts is not easily carried out due to decomposition during the preparation and its great reactivity towards oxygen. The weak emission observed in the first case may have, in part, been the result of experimental conditions. These conditions might equally well explain the failure to observe any band emission. The As-Cl band might easily exhibit its emission in the region where the OH background appears, thus making it difficult to observe. The atomic line emission should be found at 1937 Å. Observation of this line could only be made if it were extremely intense due to the lack of detector sensitivity in this region of the spectrum.

It is interesting to note the rather high bond energies of the B-O and B-F bonds, particularly in view of the fact that only band emission resulting from the BO_2 molecule was observed. It is however surprising to find that diethyl ether solutions of boron trifluoride tend to be more efficient in producing the BO_2 species than were aqueous boric acid solutions. Undoubtedly the solvent is playing a significant role in this phenomenon, but its exact nature is difficult to determine. Efficiency in aerosol formation as well as increased temperature are important factors, but the fact that the B-O and B-F bond energies are so nearly equal, leads one to the assumption that a dramatic mechanistic factor is present to account for the relative ease with which B-F bonds are converted to B-O bonds. One possible explanation for this might be associated with the fact that boron is introduced into the flame as boron trifluoride diethyl ether complex.

The sensitivities observed for boron in this study tend to suggest that the hydrogen-chlorine flame may indeed offer improved sensitivities over the conventional flame systems for boron.

The bond energies of Ba-Cl vs. Ba-O, Cs-Cl vs. Cs-O and Fe-Cl vs. Fe-O may lead one to believe that the hydrogen-chlorine flame would offer little improvement in detection limits relative to those obtained for the same elements by conventional flame techniques. The results obtained in this investigation would tend to support such a conclusion.

Considering the relative difference in the bond energies of the Cu-Cl and Cu-O bonds it is somewhat surprising to see the excellent sensitivity observed in the hydrogen-chlorine flame resulting from band emission of the Cu-Cl species. Earlier investigators (19) have also found this band to be unusually strong. In this instance the detection limit of the band nearly approaches the sensitivity exhibited by the atomic line emission in conventional flames. The presence of the OH background prevented the measurement of the atomic line emission of copper at 3247.5 Å.

Looking at the relative difference in bond energies of the Si-Cl and Si-O bonds one might anticipate that greater sensitivities for silicon might be achieved with a chlorine-hydrogen flame as opposed to conventional flames. Solutions of aqueous silicic acid and also tetramethyl silane in carbon tetrachloride failed to produce any detectable band or line emission. In view of the exceeding difficulty encountered with silicon by conventional techniques, perhaps it is

not too surprising that efforts to make such measurements in the hydrogen-chlorine flame were unsuccessful. It has been reported (12) that silicon exhibits both bands and lines in certain flames. The tendency of silicon to combine with oxygen to form one of the most stable of all diatomic molecules which does not readily dissociate accounts for the extreme difficulty in its analysis. Very few analytical flames produce sufficiently high temperatures to dissociate the Si-O bond. The temperatures found in the hydrogen-chlorine flame, being cooler than many others, is apparently not an exception to this general conclusion.

CONCLUSIONS

Summary

It was felt at the outset of this investigation that background emission in the hydrogen-chlorine flame would be better than was actually found. Nevertheless it exhibits fewer interferences than most conventional flames, and it is, in this sense, at least comparable to the oxy-hydrogen flame. Consequently it is possible to use this flame in the analysis of many elements whose line or band emission lie outside of the OH emission band region. The CuCl band is especially useful for the study of copper. Iron appears to have good potential in this respect.

Aluminum and boron analysis seem to be particularly adaptable to this system, however, it is necessary that careful selection of a suitable counter-ion be made.

In some instances the precision of the determination could be improved. In this respect it is important to recognize that the efficiency of aspiration is an important factor. Improved precision can be achieved by maintaining a constant insertion depth of the capillary in the solution. Failure to be cognizant of this can easily lead to unnecessarily large standard deviations.

It is anticipated that further improvements in the experimental and instrumental parameters will yield significantly better sensitivities than those obtained in this study.

Recommendations

Further study of this flame can be oriented towards the improvement of the background. This might be achieved by designing a better sheathing system than the one used in this study. A longer glass chimney surrounding the flame with nitrogen flowing through it might provide improved performance. The chimney should minimize the effects of turbulent air reaching the flame and thus reduce the possibility of OH formation.

It would also be of interest to study a particular element with different counter-ions in order to see more clearly how the emission is related to this important factor. Such studies might provide some significant insight into some of the mechanisms present in the flame.

Although the noisy output from the recorder was improved by using the time averaging circuit, it is felt that a premixed laminar flame could offer some real advantages in this respect. Burner design and gas regulation will be extremely important parameters if a stable flame is to be achieved.

The study of this flame can also be extended to absorption and fluorescent spectroscopy in order to determine its applicability to these important techniques. This might also lead to a better understanding of the phenomena involved in this unusual flame.

It would be also of interest to study a compound such as boron trichloride as an ether complex, in view of the lower bond energy of the B-Cl bond. Comparison of such measurements with those made upon boron trifluoride in this study might assist in explaining the results obtained in the present investigation.

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